

FGRM PT-3-1390 (REV 11-98)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE	ATTORNEY'S DOCKET NUMBER
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371			Studien 262-KGB
			U.S. APPLICATION NO. (if known, see 37 CFR 1.5) <b>09/254525</b>
INTERNATIONAL APPLICATION NO. PCT/EP97/04918	INTERNATIONAL FILING DATE 9. September 1997 (09.09.97)	PRIORITY DATE CLAIMED 13. September 1996 (13.09.96)	
TITLE OF INVENTION USE OF MICROPOROUS INORGANIC MEMBRANE CATALYSTS			
APPLICANT(S) FOR DO/EO/US Wilhelm F. Maier			
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:			
<ol style="list-style-type: none"> <li>1. <input checked="" type="checkbox"/> This is a <b>FIRST</b> submission of items concerning a filing under 35 U.S.C. 371.</li> <li>2. <input type="checkbox"/> This is a <b>SECOND</b> or <b>SUBSEQUENT</b> submission of items concerning a filing under 35 U.S.C. 371.</li> <li>3. <input checked="" type="checkbox"/> This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).</li> <li>4. <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.</li> <li>5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)) <ol style="list-style-type: none"> <li>a. <input type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau).</li> <li>b. <input checked="" type="checkbox"/> has been transmitted by the International Bureau.</li> <li>c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).</li> </ol> </li> <li>6. <input checked="" type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)).</li> <li>7. <input type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)) <ol style="list-style-type: none"> <li>a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau).</li> <li>b. <input type="checkbox"/> have been transmitted by the International Bureau.</li> <li>c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.</li> <li>d. <input type="checkbox"/> have not been made and will not be made.</li> </ol> </li> <li>8. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).</li> <li>9. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).</li> <li>10. <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).</li> </ol>			
Items 11. to 16. below concern document(s) or information included:			
<ol style="list-style-type: none"> <li>11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.</li> <li>12. <input checked="" type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.</li> <li>13. <input checked="" type="checkbox"/> A FIRST preliminary amendment. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment.</li> <li>14. <input type="checkbox"/> A substitute specification.</li> <li>15. <input type="checkbox"/> A change of power of attorney and/or address letter.</li> <li>16. <input checked="" type="checkbox"/> Other items or information:  COPY OF PUBLISHED APPLN. WO 98/10865 (GERMAN)  COPY OF INTL SEARCH REPORT (PCT/ISA/210) (GERMAN &amp; ENGLISH)  COPY OF PCT REQUEST (PCT/RO/101) (GERMAN)  COPY OF INTL. PRELIM. EXAM. REPORT (PCT/IPEA/409) (GERMAN)  COPY OF WRITTEN OPINION (PCT/IPEA/408) (GERMAN)  COPY OF NOTIFICATION OF TRANS. OF INTL. S.R. (PCT/IPEA/220) (GERMAN)  COPY OF PCT DEMAND (PCT/IPEA/401) (GERMAN)  COPY OF LETTER OF JULY 6, 1998 WITH SUBSTITUTE CLAIMS 1-3 (GERMAN)  COPY OF SUBSTITUTE CLAIMS 1-3 (ENGLISH)  VERIFIED STATEMENT CLAIMING SMALL ENTITY STATUS  2 SHEETS OF DRAWINGS </li> </ol>			

17. ☒ The following fees are submitted:**BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):**

Search Report has been prepared by the EPO or JPO ..... \$840.00

International preliminary examination fee paid to USPTO (37 CFR 1.482) ..... \$670.00

No international preliminary examination fee paid to USPTO (37 CFR 1.482)  
but international search fee paid to USPTO (37 CFR 1.445(a)(2)) ..... \$760.00Neither international preliminary examination fee (37 CFR 1.482) nor  
international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... \$970.00International preliminary examination fee paid to USPTO (37 CFR 1.482)  
and all claims satisfied provisions of PCT Article 33(2)-(4) ..... \$96.00**ENTER APPROPRIATE BASIC FEE AMOUNT =****CALCULATIONS** PTO USE ONLY

\$ 840.00

Surcharge of \$130.00 for furnishing the oath or declaration later than ☐ 20 ☐ 30  
months from the earliest claimed priority date (37 CFR 1.492(e)).

\$

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE
Total claims	3 - 20 =		x \$18.00
Independent claims	1 - 3 =		x \$78.00

\$

\$

\$

MULTIPLE DEPENDENT CLAIM(S) (if applicable) + \$260.00

\$ 840.00

**TOTAL OF ABOVE CALCULATIONS =**Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement  
must also be filed (Note 37 CFR 1.9, 1.27, 1.28).

\$ 420.00

**SUBTOTAL =**

\$ 420.00

Processing fee of \$130.00 for furnishing the English translation later than ☐ 20 ☐ 30  
months from the earliest claimed priority date (37 CFR 1.492(f)).

\$

+

**TOTAL NATIONAL FEE =**

\$

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be  
accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +

\$

+

**TOTAL FEES ENCLOSED =**

\$

Amount to be:  
refunded

\$

charged

\$ 420.00

a. ☐ A check in the amount of \$ \_\_\_\_\_ to cover the above fees is enclosed.b. ☒ Please charge my Deposit Account No. 19-3869 in the amount of \$ 420.00 to cover the above fees.  
A duplicate copy of this sheet is enclosed.c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any  
overpayment to Deposit Account No. 19-3869. A duplicate copy of this sheet is enclosed.**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

## SEND ALL CORRESPONDENCE TO:

Kurt G. Briscoe  
SPRUNG KRAMER SCHAEFER & BRISCOE  
660 WHITE PLAINS ROAD  
TARRYTOWN, NY 10591

SIGNATURE:

Kurt G. Briscoe

NAME

33,141

REGISTRATION NUMBER

Applicant or Patentee: Wilhelm F. Maier et al Attorney KGB

Serial or Patent No. : \_\_\_\_\_ Docket No.: Studien 262-KGB

Filed or Issued: \_\_\_\_\_

For: Use of Microporous Inorganic Membrane Catalysts

**VERIFIED STATEMENT (DECLARATION) CLAIMING SMALL ENTITY  
STATUS (37 CFR 1.9(f) AND 1.27(d) - NONPROFIT ORGANIZATION**

I hereby declare that I am an official empowered to act on behalf of the nonprofit organization identified below:

NAME OF ORGANIZATION Studiengesellschaft Kohle mbH

ADDRESS OF ORGANIZATION Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr,  
Germany

TYPE OF ORGANIZATION Trustee for the Max-Planck-Institut für Kohlenforschung,  
Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr, DE

☐ University or other institution of higher education

I hereby declare that the nonprofit organization identified above qualifies as a nonprofit organization as defined in 37 CFR 1.9(e) for purposes of paying reduced fees under section 41(a) and (b) of Title 35, United States Code with regard to the invention entitled see above by inventor(s) W.F. Maier described in

- ☒ the specification filed herewith  
☐ application Serial No. \_\_\_\_\_, filed \_\_\_\_\_  
☐ patent no. \_\_\_\_\_, issued \_\_\_\_\_

I hereby declare that rights under contract or law have been conveyed to and remain with the nonprofit organization with regard to the above identified invention.

If the rights held by the nonprofit organization are not exclusive, each individual, concern or organization having rights to the invention is listed below\* and no rights to the invention are held by any person, other than the inventor, who could not qualify as a small business concern under 37 CFR 1.9(d) or by any concern which would not qualify as a small business concern under 37 CFR 1.9(d) or a nonprofit organization under 37 CFR 1.9(e). \*NOTE: Separate verified statements are required from each named person, concern or organization having rights to the invention averring to their status as small entities. (37 CFR 1.27)

FULL NAME \_\_\_\_\_

ADDRESS \_\_\_\_\_

☐ INDIVIDUAL                      ☐ SMALL BUSINESS CONCERN                      ☐ NONPROFIT ORGANIZATION

FULL NAME \_\_\_\_\_

ADDRESS \_\_\_\_\_

☐ INDIVIDUAL                      ☐ SMALL BUSINESS CONCERN                      ☐ NONPROFIT ORGANIZATION

I acknowledge the duty to file, in this application or patent, notification of any change in status resulting in loss of entitlement to small entity status prior to paying, or at the time of paying, the earliest of the issue fee or any maintenance due after the date on which status as a small entity is no longer appropriate. (37 CFR 1.28).

SCANNED 2 I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements may jeopardize the validity of the application, any patent issuing thereon, or any patent to which this verified statement is directed.

Prof. Dr. E. Ziegler

NAME OF PERSON SIGNING

NAME OF PERSON SIGNING

Studiengesellschaft Kohle mbH

TITLE OF ORGANIZATION

TITLE OF ORGANIZATION

Kaiser-Wilhelm-Platz 1,  
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ADDRESS OF PERSON SIGNING

ADDRESS OF PERSON SIGNING

E. Ziegler  
SIGNATURE

SIGNATURE

February 23, 1999

Date

Date

09/254525

369 Rec'd PCT/PTO 08 MAR 1999

Studien 262-KGB:lad  
Zi/D

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicants : Wilhelm F. MAIER  
Serial No. : TBA  
Filed : Herewith  
For : USE OF MICROPOROUS INORGANIC MEMBRANE  
CATALYSTS  
Group Art Unit : TBA  
Examiner : TBA

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March 8, 1999

Hon. Commissioner for Patents  
Washington, D.C. 20231

**PRELIMINARY AMENDMENT**

Prior to examination, kindly amend the above-identified application as follows:

**IN THE CLAIMS**

Cancel all the claims and substitute:

--4. A process for performing a catalyzed chemical reaction of starting materials using an amorphous microporous membrane, wherein said starting materials are pressed through the pores of said membrane containing

catalytically active components, wherein the diameter of said pores are not larger than twice the diameter of the molecules of said starting materials, and the overall distribution of pore diameters has a half-width of  $< 0.3$  nm.--

--5. The process according to claim 1, wherein said pore diameter is between 0.5 and 5 nm.--

--6. The process according to claim 1, wherein the thickness of the amorphous layer of said membrane is  $< 10$   $\mu$ m, preferably  $< 2$   $\mu$ m.--

#### **REMARKS**

The foregoing amendment serves to clear up any potential confusion concerning which claims are pending in the case and also to place the claims in better form for U.S. examination.

Early and favorable action is earnestly solicited.

Respectfully submitted,

SPRUNG KRAMER SCHAEFER & BRISCOE

By: 

Kurt G. Briscoe  
Reg. No. 33,141

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Studien 262-KGB  
Zi/D

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicants : Wilhelm F. MAIER  
Serial No. : 09/254,525  
Filed : March 8, 1999  
For : USE OF MICROPOROUS INORGANIC MEMBRANE CATALYSTS  
Art Unit : To Be Assigned  
Examiner : To Be Assigned

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March 17, 1999

Hon. Assistant Commissioner  
for Patents  
Washington, D.C. 20231

**SECOND PRELIMINARY AMENDMENT**

Sir:

Prior to examination, kindly amend the above-identified application as follows:

**IN THE CLAIMS**

Please amend claims 5 and 6 as follows:

5. (Once Amended) The process according to claim [1]4, wherein said pore diameter is between 0.5 and 5 nm.

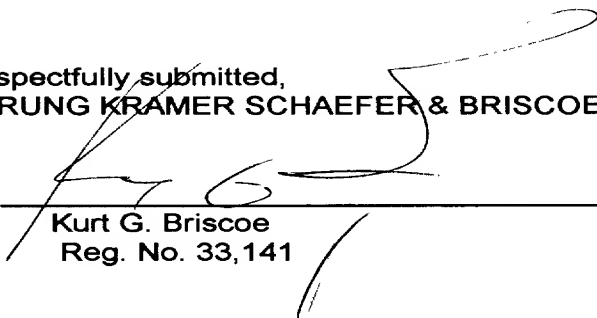
6. (Once Amended) The process according to claim [1]4, wherein the thickness of the amorphous layer of said membrane is  $< 10 \mu\text{m}$ , preferably  $< 2 \mu\text{m}$ .

**REMARKS**

The foregoing amendment serves to correct minor claim dependencies not effecting the scope of the claims.

Early and favorable action is earnestly solicited.

Respectfully submitted,  
SPRUNG KRAMER SCHAEFER & BRISCOE

By:   
Kurt G. Briscoe  
Reg. No. 33,141

KGB:lf

660 White Plains Road  
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(914) 332-1700

I hereby certify that this correspondence is being deposited with the United States Postal Services as first class mail in an envelope addressed to The Assistant Commissioner for Patents, Washington, D.C. 20231 on March 17, 1999.

SPRUNG KRAMER SCHAEFER & BRISCOE

Date March 17, 1999  
STUD262.3

By 



C L A I M S :  
(substitute sheet)

1. A process for performing a catalyzed chemical reaction of starting materials using an amorphous microporous membrane, characterized in that said starting materials are pressed through the pores of said membrane containing catalytically active components, wherein the diameters of said pores are not larger than twice the diameter of the molecules of said starting materials, and the overall distribution of pore diameters has a half-width of  $< 0.3$  nm.
  2. The process according to claim 1, wherein said pore diameter is between 0.5 and 5 nm.
  3. The process according to claim 1, wherein the thickness of the amorphous layer of said membrane is  $< 10$   $\mu\text{m}$ , preferably  $< 2$   $\mu\text{m}$ .
-

2 PRTS

09/254525

300 Rec'd PCT/PTO 08 MAR 1999

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### Use of Microporous Inorganic Membrane Catalysts

Consecutive and side reactions are the main cause of reduced yields and the production of chemical waste and side products in chemical production. It has now been found that undesired consecutive and side reactions can be suppressed and even completely prevented by the use of microporous membrane catalysts.

Mounting environmental restrictions and costs increasingly augment the demands on chemical production. More than 90% of the chemical products require heterogeneous catalysts in one or more steps.

A new development in research for improving chemical processes is directed to membrane catalysts. These are preferably inorganic, catalytically active membranes which have the advantage, as compared to organic membranes, of higher thermal, chemical and mechanical resistance and, in principle, unlimited capability of regeneration and sterilizability, and of being usable at higher temperatures as well. Their use improves chemical production processes through a combination of separation properties and catalytic properties. Thus, membranes can be used to change the way of performing a reaction so that the liquid or gaseous reactants separately flow over the two sides of the membrane and thus a reaction zone can form only in the interior of the membrane. The principles and characteristics of such membrane reactors known to date have been published in several review articles (J.N. Armor, Appl. Catal. 49 (1989), 1; H.P. Hsieh, Catal. Rev. Sci. Eng. 33 (1991), 1; M.P. Harold, P.

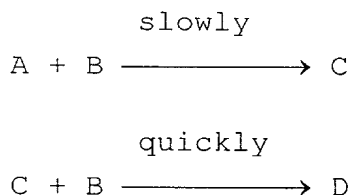
Cini, B. Patenaude und K. Venkataraman, AIChE Symp. Ser. 85 (268), 26 (1889)).

The preferential permeation of one reactant in porous membranes can be used to increase selectivity (G. Saracco, V. Specchia, Catal. Rev. Sci. Eng. 36 (1994), 305). In most cases, attempts are made to improve reaction equilibria and thus selectivities and yields by selectively separating one of the products of selectively adding one of the starting materials.

Surprisingly, in contrast to previous membrane applications, it has now been found that undesirable consecutive and side reactions in various chemical reactions can be selectively suppressed by the use of microporous membrane catalysts if the pore size of the membrane is but slightly larger than the reactants and if the reaction is performed by pressing the reaction mixture through the membrane. In the interior of the membrane, the catalytically active sites of the membrane must be preferably localized on the inner surface of the pores. Significant reactivity on the outer membrane surface adversely affects selectivity. The invention herein described is distinct from the mentioned membrane applications and others known from the literature mainly in that the membrane is not employed for permeability-selective enrichment or depletion of products, educts or catalyst poisons, but two or more mutually reacting educts are pressed together in the same direction through the catalytically active membrane. Due to the particular nanostructure of the membrane and the way of performing the reaction, the molecules are isolated in the pores and thus consecutive reactions are prevented. Thus, this membrane application for the first time allows complete separation of the product molecules from the starting materials during their generation already. This is separation in molecular dimensions which is thus distinct in principle from the activity of known larger-pore membranes.

The preparation of the coating solutions of the microporous catalyst membranes is performed according to the preparation of the mixed oxide catalysts as described in DE-A-195 45 042.6 and PCT/EP 96/00766. In all other respects, the membrane preparation is according to the methods described in US PS 5,492,873 and US 5,250,184. From those applications, it cannot be seen that a novel effective method for preventing consecutive reactions is obtained if the way of performing the reaction is changed and reactants are used which are but slightly smaller than the pores of the membrane.

The mechanism of suppressing consecutive reactions with membrane catalysts can be illustrated as follows. A reactant molecule A (e.g., hydrocarbon) reacts with a reactant B (e.g., oxygen) at the active site of the catalyst to form the desired product, molecule C (e.g., an alcohol). However, molecule C is more reactive than A (e.g., an alcohol is known to be more reactive than a hydrocarbon) and now preferably reacts with more B to quickly form consecutive products D (e.g., ketones, carboxylic acids, diols, etc., to the final products carbon dioxide and water).



This problem is known for many selective oxidation, hydrogenation and halogenation reactions and is circumvented in technology by performing the reaction with substoichiometric amounts of B with low conversions of A and short residence times. The problem is caused by the back mixing with the desired product C, which is unavoidable when the reaction is performed in the conventional way.

Such back mixing can be prevented, however, if the reaction takes place within the pores of a membrane and the pore size is not larger than twice the kinetic diameter of these molecules. Since most molecules used for heterogeneous catalysis have a size of between 0.3 and 1.5 nm, pore sizes of at least 0.6 to a maximum of 3 nm are required, depending on the molecular size. It is essential that the required pore size has a very narrow distribution and that enough catalytically active sites are present on the interior surface of such pores.

Figure 1 illustrates the effect of such pores. Above the membrane, there is the mixture/solution of the two reactants A and B. Now, the latter flow together through the pores, with the size of the pores preventing a significant change of the mixture's nature during such diffusion. If neighboring A and B molecules reach an active site during such diffusion, conversion to C may occur. If C, in the further course of diffusion until exiting from the pore, reaches other catalytically active sites, further conversion can no longer occur since there is no more B in close proximity, and additional B cannot be supplied due to the limited pore dimensions. Thus, any kinetically and thermodynamically favored consecutive reaction is prevented, and a high selectivity for the desired molecule C is achieved. This effect of prevented back mixing is clearly achievable only for the correct pore sizes of the membrane. If the pores are too large or if the pore size distribution is too broad, product selectivity is adversely affected by uncontrolled diffusion effects.

The reactor herein employed is depicted in Figure 2. The reaction can be performed correspondingly in any membrane reactor, such as tubular reactors, capillary reactors and capillary bundle reactors.

In the Examples set forth below, the selective hydrogenations, selective oxidations and selective alkylations are performed on

another 10 min of stirring 0.3 ml of conc. HCl. The Pt salt is added to the mixture with stirring, and the mixture is again diluted with 10 ml of ethanol. The mixture is subsequently stirred for several hours.

1b) Preparation of a single-coated catalyst membrane:

The catalyst is applied as a thin film to a commercially available ceramic membrane by dip coating. In this Example, a commercially available asymmetric ceramic membrane with the following characteristics was used: material:  $\text{Al}_2\text{O}_3$ , diameter of disks: 47 mm, thickness: 2 mm, thickness of separation layer: 1.5  $\mu\text{m}$ , average pore diameter: 4.5 nm. The pore sizes and pore size distributions are determined by recording the adsorption isotherm at the temperature of liquid argon or liquid nitrogen. The ceramic disks are first refluxed in a mixture of isopropanol/acetone for 4 h and subsequently dried in an oven at 400 °C for 12 h. The thus cleaned disks are coated as follows.

The ceramic disk is covered with adhesive tape on the large-pore side, attached to a thread and immersed in the above sol-gel solution 1a. In a saturated ethanol atmosphere (closed apparatus), the membrane is withdrawn from the solution with a pulling speed of 0.45 cm/min in a vibrationless way. The ceramic membrane is thereby coated with a thin gel film. After the membrane has been completely withdrawn from the solution, the thread is detached from the coupler and attached to the lid with adhesive tape. The membrane is now suspended at about 2 cm over the beaker. The latter is removed by briefly lifting the cylinder. After the beaker has been removed, 5 ml of ethanol is injected in the cylinder, and the membrane is subsequently left suspended in the alcohol atmosphere for 5 days. Thereafter, the membrane is removed and mildly calcined. In order to obtain thin films free of cracks, the membrane is dried according to the following temperature schedule: 0.1 °C/min heating rate until  $T = 65^\circ\text{C}$ , maintaining at  $T = 65^\circ\text{C}$  for 100 min, 0.1 °C/min

heating rate until  $T = 250^{\circ}\text{C}$ , maintaining at  $T = 250^{\circ}\text{C}$  for 300 min, cooling ( $10^{\circ}\text{C}/\text{min}$ ) to room temperature. The remaining coating solution can be stored in a deep freezer for further coatings, or further used for the preparation of powdery catalysts.

1c) Preparation of a triple-coated catalyst membrane:

For increasing the layer thickness, the coating as described under 1b) was performed three times.

1d) Preparation of a comparative powdery Pt catalyst

The remaining coating solution from 1b or 1c was allowed to stand at room temperature for 10 h and then dried and calcined as described under 1b. The thus produced coarse glass powder is milled to the required grain size in a powder mill and employed as a powder catalyst.

Example 2

Selective hydrogenation of 2-hexyne in a membrane reactor with membrane 1b at  $50^{\circ}\text{C}$

The single-coated membrane prepared according to the above method 1b was incorporated in a membrane reactor and activated under hydrogen flow ( $10\text{ ml}/\text{min}$ ) at a temperature of  $200^{\circ}\text{C}$  for 12 h. Then, the temperature was decreased to the reaction temperature ( $50^{\circ}\text{C}$  in this case). The reactor was filled with 10 ml of n-decane, and 200  $\mu\text{l}$  of 2-hexyne was added. The mixture was then stirred for 2 min. The vessel was pressurized with hydrogen from above (hydrogen flow of  $30\text{ ml}/\text{min}$  when a bubble counter was connected above the solution). The reactor was hermetically sealed. At a conversion of 22%, only 2- and 3-hexenes, but no 1-hexene and no n-hexane could be detected in the permeate (sensitivity  $< 0.1\%$ ).

a wide variety of membranes, such as hydrophilic and hydrophobic, Pt- and Pd-containing, amorphous  $\text{TiO}_2$  membranes, microporous hydrophobic V-Si-Ti mixed oxide membranes and acidic Al-Si mixed oxide membranes.

For completely suppressing back mixing, all membranes are suitable as long as they have a monomodal microporosity, active sites within the pores, and a narrow pore size distribution with pore diameters of not smaller than 0.5 nm and not larger than 3 nm. These include suitable organic membranes and defectless zeolite membranes. As the reactions the selectivity of which can be improved by the prevention of back mixing, there may be mentioned oxidation reactions, hydrogenation reactions, chlorination reactions, bromination reactions, fluorination reactions, addition reactions, cycloaddition reactions, oligomerization reactions, dimerization reactions, aromatic and aliphatic alkylation and acylation reactions, redox reactions, pericyclic reactions, substitution reactions, cyclizations, hydrolytic reactions, elimination reactions, esterifications and etherifications.

#### Example 1

Preparation of a hydrophobic Pt-containing catalyst membrane:

##### 1a) Preparation of the coating solution:

In a 20 ml beaker, 0.105 g of  $\text{Na}_2\text{PtCl}_6$  is dissolved in 10 ml of ethanol with stirring. In a 100 ml beaker, 9.5 ml of distilled titanium(IV) isopropoxide is provided under argon, and then 2.5 ml of methyltriethoxysilane (MTS) is added with stirring. Now, 40 ml of distilled ethanol (10 ml each of ethanol in intervals of 5 min) is added to the beaker. After 10 min of stirring, the following amounts of acid are successively added: 0.1 ml of 8 N HCl, after 2 min of stirring 0.1 ml of conc. HCl, after another 5 min of stirring 0.3 ml of conc. HCl, after

SCANNED 2



### Example 3

Selective hydrogenation of 2-hexyne in a membrane reactor with membrane 1b at 110 °C

The experiment was performed as described in Example 2. At a reaction temperature of 110 °C, a conversion of more than 60% was observed in the permeate. Again, no n-hexane and no 1-hexene could be detected in the permeate, and only isomeric hexenes were formed as products.

### Example 4

Selective hydrogenation of 2-hexyne in a membrane reactor with the triple-coated membrane 1c at 110 °C

The experiment was performed as described in Example 2, but using membrane 1c. In the permeate, a 2-hexyne conversion of more than 60% was achieved. Again, no n-hexane and no 1-hexene could be detected in the permeate, and only isomeric hexenes were formed as products.

### Example 5

Selective hydrogenation of 1,3-hexadiene in a membrane reactor with membrane 1b at 110 °C

The single-coated membrane prepared according to the above method 1b was incorporated in a membrane reactor and activated under hydrogen flow (10 ml/min) at a temperature of 200 °C for 12 h. Then, the temperature was decreased to 90 °C. The reactor was filled with 10 ml of n-decane, and 200 µl of 1,3-hexadiene was added. The mixture was then stirred for 2 min. The vessel was pressurized with hydrogen from above (hydrogen flow of 30 ml/min when a bubble counter was connected above the solution). The reactor was hermetically sealed. At a conversion of

> 80%, only trans-2-hexene and cis-3-hexene (15:85), but no 1-hexene and no n-hexane could be detected in the permeate (sensitivity < 0.1%).

#### Example 6

##### Hydrogenation of 2-hexyne in a batch reactor

Catalyst 1d was activated under hydrogen flow at 200 °C before the reaction was begun. In 50 ml of n-decane, 0.5 ml of 2-hexyne and 100 mg of catalyst 1d (grain size < 100 µm) were stirred at 2000 rpm in a batch reactor (150 ml flask) at 90 °C under an H<sub>2</sub> atmosphere. The course of the reaction was followed with a gas chromatograph. Even at conversions as low as 4%, more than 70% of the product was n-hexane, 26% was 2-hexene, and 4% was trans-3-hexene.

#### Example 7

##### Hydrogenation of 1,3-hexadiene in a batch reactor

Catalyst 1d was activated under hydrogen flow at 200 °C before the reaction was begun. In 50 ml of n-decane, 0.5 ml of 1,3-hexadiene and 100 mg of catalyst 1d (grain size < 100 µm) were stirred at 2000 rpm in a batch reactor (150 ml flask) at 90 °C under an H<sub>2</sub> atmosphere. The course of the reaction was followed with a gas chromatograph. Here again, even at conversions of < 10%, n-hexane was the prevailing product.

#### Example 8

##### Preparation of a Pd-containing TiO<sub>2</sub> membrane

The preparation of the coating solution was performed according to description 1a, except that 0.035 g of Pd(II) acetylacetonate (21.5 mmol) was employed instead of Na<sub>2</sub>PtCl<sub>6</sub>. The prepara-

b) Membrane preparation

In a 150 ml polypropylene beaker, 20 ml of TEOS (0.0783 mol) is dissolved in 25 ml of ethanol, and a solution of 4 ml of H<sub>2</sub>O and 0.87 g of Al(NO<sub>3</sub>)<sub>3</sub> (2.3 mmol) is added dropwise.

The solution is stirred for 5 min and then acidified with 500 µl of BF<sub>3</sub>/acetate complex. With the thus obtained sol-gel solution, the precoated membrane is coated according to the dip coating method 1b. The membrane is subsequently dried under an ethanolic atmosphere for 5 days and mildly calcined. To minimize back mixing, the active aluminum-containing layer is again coated with an inactive SiO<sub>2</sub> layer according to 10a.

Example 11

Ethylation of biphenyl with ethanol on catalyst membrane 10

The membrane prepared by the above method 10 was incorporated in a membrane reactor and heated under argon flow (290 ml/min) at 1°C/min to a reaction temperature of 250°C. Biphenyl was heated at 140°C in a separate solid evaporator and continuously evaporated and passed through the membrane with an ethylene gas flow of 10 ml/min. The permeate was cooled with dry ice, and the solids obtained were analyzed with GC. Only monoethylated biphenyls were obtained as the product.

The isomer distribution is 41% 2-ethylbiphenyl, 32% 3-ethylbiphenyl, and 27% 4-ethylbiphenyl.

### Example 12

Preparation of a hydrophobic vanadium-containing catalyst membrane

The asymmetric support membrane is coated according to Example 1. For preparing the coating solution, 1.9 g of vanadium(II) acetylacetonate, 25.3 ml of TEOS, 9.7 ml of MTES, 29.0 ml of EtOH, and 7.21 ml of 8 N HCl was stirred in a PP beaker for 1 h, and the coated membrane was prepared as described under 1b.

### Example 13

Selective cyclohexane oxidation on catalyst membrane 12 with TBHP

Membrane 12 was incorporated in a membrane reactor and treated by heating over night under Ar flow at 200 °C and then cooled to 90 °C. Onto the membrane, 3.04 ml of cyclohexane and 6.95 ml of TBHP (3 M solution in isooctane) was added (molar ratio of TBHP to cyclohexane = 2/1). At a conversion of 70%, only cyclohexanol and cyclohexanone at a ratio of 1:1 were present in the permeate. By increasing the flow rate, a reduction of conversion and an increase of the ratio of cyclohexanol/cyclohexanone up to 1.7 was achieved.

### Example 14

Epoxidation of 1-octene with TBHP in a membrane reactor with membrane 12

The membrane reactor with inserted vanadium-containing membrane 12 was heated to 200 °C at 1 °C/min. At the same time, it was purged with argon at 90 °C. The reactor temperature was maintained for 1 h. Then, the reactor was allowed to cool to room

temperature at 0.1 °C/min under argon flow. 1-Octene (47.4 mmol, 5.32 g, 7.44 ml) and t-butylhydroperoxide (3M, anhydrous in isooctane, 9.0 mmol, 2.27 g, 3.00 ml) were successively added to the reactor. The reactor was sealed and heated to 80 °C with stirring (300 rpm). Samples were taken through the sampling valve below the membrane.

At a conversion of 11%, the permeate showed a product selectivity of > 99% for 1-epoxyoctane, the only product.

#### Example 15

Preparation of a hydrophilic microporous Pt-containing catalyst membrane

a) In a 20 ml beaker, 0.105 g of  $\text{Na}_2\text{PtCl}_6$  is dissolved in 10 ml of ethanol with stirring.

In a 100 ml beaker, 12 ml of distilled titanium(IV) isopropoxide is provided under argon and stirred. Now, 40 ml of distilled ethanol (10 ml each of ethanol in intervals of 5 min) is added. After 10 min of stirring, the following amounts of acid are successively added: 0.1 ml of 8 N HCl, after 2 min of stirring 0.1 ml of conc. HCl, after another 5 min of stirring 0.3 ml of conc. HCl, after another 10 min of stirring 0.3 ml of conc. HCl. The Pt salt is added to the mixture with stirring, and the mixture is again diluted with 10 ml of ethanol. The mixture is subsequently stirred for several hours.

b) A precoated membrane as described under 10a is employed as the support membrane. The membrane preparation was performed with coating solution 16a, but otherwise as described under 1b.

### Example 16

Selective hydrogenation of 2-hexyne in a membrane reactor with membrane 16 at 60 °C

2-Hexyne was reacted on the membrane as described under 2 at a reaction temperature of 60 °C. At a conversion of 10%, *cis*-2-hexene could be detected in the permeate as the only product.

C L A I M S :

1. Amorphous microporous membranes having pore sizes of from 0.5 to 2 nm with a layer thickness of below 10  $\mu\text{m}$  and a half-width of  $< 0.3$  nm and containing in their pores at least one catalytically active component for heterogeneously catalyzed reactions, wherein two or more mutually reacting starting materials are simultaneously pressed in one direction through the catalytic membrane.
2. The membrane catalysts according to claim 1, characterized in that said pore size is not larger than twice the diameter of the molecules of said starting materials, especially from 0.6 to 3 nm, with a thickness of the amorphous layer of from 0.1 to 10  $\mu\text{m}$ , preferably  $< 2$   $\mu\text{m}$ , wherein two or more reactants are passed through the membrane, which involves the avoiding of back mixing.

A b s t r a c t

To avoid side reactions in the catalytic reaction of two or more reactants, the mutually reacting starting materials are simultaneously passed in the same direction through a micro-porous catalyst membrane, the pore size of the membrane being selected within the range of dimensions of the reactant molecules.



Figure 1

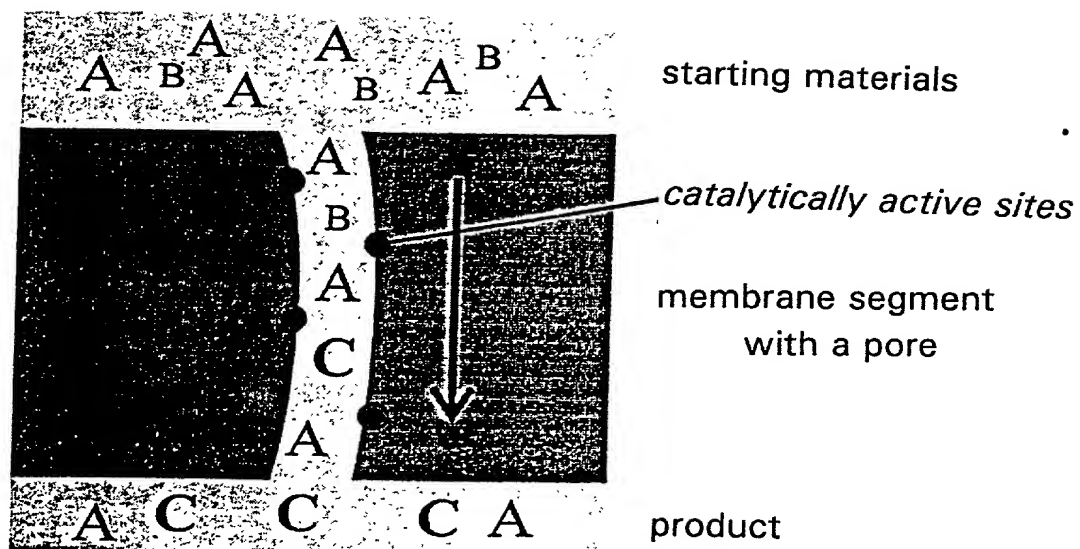
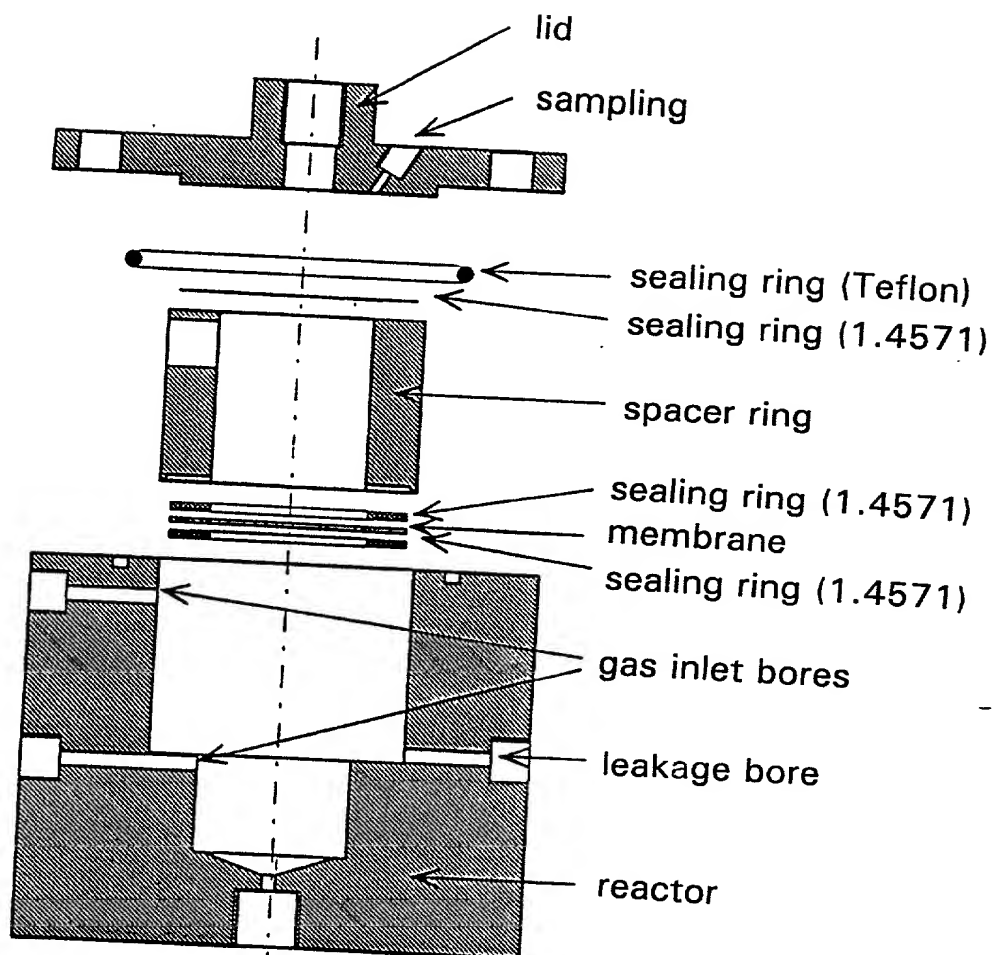


Figure 2



# COMBINATION DECLARATION & POWER OF ATTORNEY

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name, —

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

Use of Microporous Inorganic Membrane Catalysts

the specification of which

☒ is attached hereto.

☐ was filed on \_\_\_\_\_ as  
application Serial No. \_\_\_\_\_.

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations §1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s)

Priority Claimed

196 37 365.4  
(Number)

DE  
(Country)

13/09/1996  
(Day/Month/Yr. Filed)

☒ yes [ ] no

\_\_\_\_\_  
(Number)

\_\_\_\_\_  
(Country)

\_\_\_\_\_  
(Day/Month/Yr. Filed)

[ ] yes [ ] no

I hereby claim the benefit of 35 U.S.C. § 119(e) of any United States Provisional Application(s) listed below.

\_\_\_\_\_  
(application number)

\_\_\_\_\_  
(filing date)

\_\_\_\_\_  
(application number)

\_\_\_\_\_  
(filing date)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

PCT/EP97/04918  
(Application Serial No.)

09/09/1997  
(Filing Date)

pending  
(Status)  
(patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punished by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith:

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INVENTOR'S SIGNATURE: \_\_\_\_\_ DATE: \_\_\_\_\_  
RESIDENCE: \_\_\_\_\_ CITIZENSHIP: \_\_\_\_\_

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INVENTOR'S SIGNATURE: \_\_\_\_\_ DATE: \_\_\_\_\_  
RESIDENCE: \_\_\_\_\_ CITIZENSHIP: \_\_\_\_\_

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